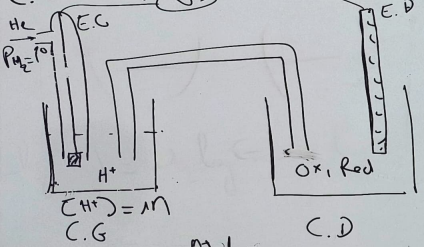


Potentiel de l'électrode : E (V/E.S.H.)
 Ox / Red

demie - pile $E_{H^+ / H_2}^\ominus = E_G^\ominus = 0V$
 C.D : Ox / Red à étudier

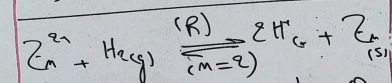
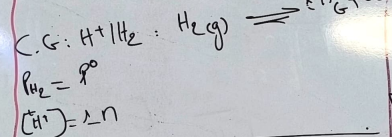
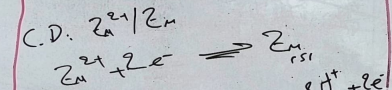
C.G : Couple de référence : H^+ / H_2
 (E.S.H.)



S Ox / Red : n / m (sd) : Electrode droite M_{sd}

S (Ox)_{op} / (Red)_{op} : Electrode droite (Pt)

$$E_x : Z_n^{2+} / Z_m$$



$$\Delta_r G_m = \Delta_r G_m^\ominus + RT \ln Q_m$$

Formule de Nernst : $\Delta_r G_m = -mFDE$
 $\Delta_r G_m^\ominus = -mFDE^\ominus$

$$DE = E_D - E_G$$

$$DE^\ominus = E_D^\ominus - E_G^\ominus$$

$$E_D - E_G = E_{V(E.S.H.)}^{Ox / Red} ; E_D^\ominus - E_G^\ominus = E_{V(E.S.H.)}^{Ox / Red}$$

$$-mFDE = -mFDE^\ominus + RT \ln Q_m$$

$$DE = DE^\ominus - \frac{RT}{mF} \ln Q_m$$

$$DE = DE^\ominus - \frac{0,06}{n} \log Q_m$$

$$DE = DE^\ominus - \frac{0,06}{n} \log \frac{[H^+]_G^2}{[Z_n^{2+}] \cdot \frac{P_{H_2}}{P^\ominus}}$$

$$n[H^+]_G = 1M ; P_{H_2} = P^\ominus$$

$$DE = DE^\ominus + \frac{0,06}{2} \log [Z_n^{2+}]$$

$$E_{V(E.S.H.)}^{Z_n^{2+} / Z_m} = E_{V(E.S.H.)}^{Ox / Red} + 0,03 \log [Z_n^{2+}]$$

$$\frac{RT}{F} \ln x = 0,06 \log x$$

Mesure de $E_{Z_n^{2+} / Z_m}^\ominus$
 demie - pile standard
 $[Z_n^{2+}] = 1M$

$$E_{V(E.S.H.)}^{Ox / Red}^{Z_n^{2+} / Z_m} = E_{V(E.S.H.)}^{Z_n^{2+} / Z_m}$$

$$\Delta_r H_m^\ominus - T \Delta_r S_m^\ominus$$

$$\sum \nu_L D_L G_L^\ominus - \sum \nu_R D_R G_R^\ominus$$

$$\Delta_r G_m^\ominus$$

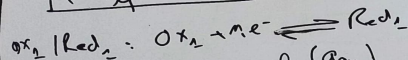
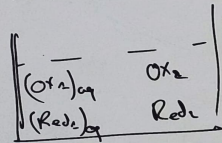
$$\sum \nu_L P_L^\ominus - \sum \nu_R P_R^\ominus$$

$$-RT \ln K_m$$

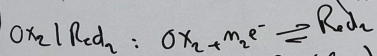
(R) : Reaction Ox-Red
 $\Delta_r G_m^\ominus = -mFDE^\ominus$

Potentiel delec. Inad. : $E(V/E.S.H)$
 OX/Red

Reactions below $OX-Red$

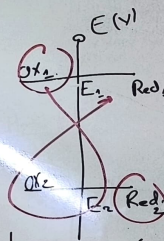


$$E_1 = E_1^0 + \frac{0.06}{m_1} \log \frac{(a_{OX_2})}{(a_{Red_2})}$$



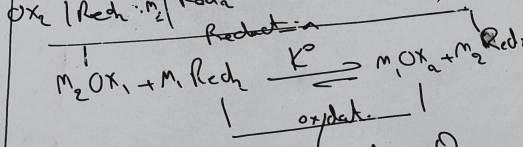
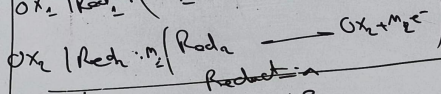
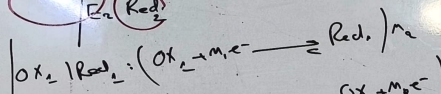
$$E_2 = E_2^0 + \frac{0.06}{m_2} \log \frac{(a_{OX_2})}{(a_{Red_2})}$$

On suppose $E_1 > E_2$



$m = P.P.(n(m_1, m_2))$
 (m_1, m_2) premiers entre eux

$$m = m_1 \times m_2$$



$$\Delta_r G(r) = \Delta_r G^0(r) + RT \ln Q$$

$$-mFDE = -mFDE^0 + RT \ln Q$$

$$DE = DE^0 - \frac{RT}{mF} \ln Q$$

$$DE = DE^0 - \frac{0.06}{m} \log Q$$

à l'équilibre $\Delta_r G(r) = 0 \Rightarrow (Q(r))_{eq} = K^0(r)$
 $\Delta_r G^0 + RT \ln K^0(r) = 0$

à l'équilibre $\Delta_r G(r) = 0$
 $\Delta_r G^0 = 0$
 $Q(r) = K^0(r)$

$$DE^0 - \frac{0.06}{m} \log K^0(r) = 0$$

$$K^0(r) = 10^{\frac{mDE^0}{0.06}}$$

$$m = P.P.(n(m_1, m_2))$$

$R_g : \Sigma OX_2 \rightleftharpoons Red_2$
 $(A) / B ; C / (A)$

(R): réaction de dismutation

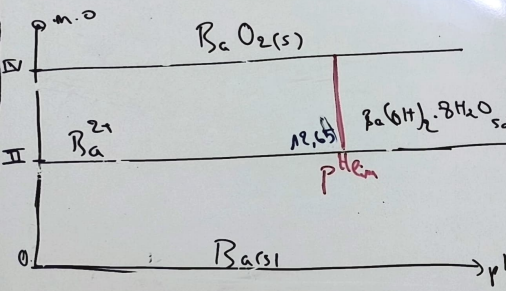
$\Rightarrow A$ se dismute pour donner B et C

$R = 8,314 \text{ J.K}^{-1} \text{ mol}^{-1}$ Série E-pH

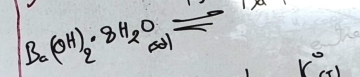
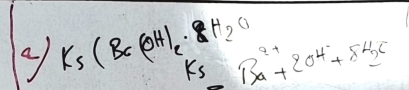
Ex^{n°1} $C_{\text{Tba}} = 10^{-4} \text{ mol.L}^{-1}$

1)

espèce	Ba_{cs}	Ba^{2+}	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}_{\text{sd}}$	$(\text{BaO}_2)_\text{s}$
m.o	0	II	II	IV



pH ? ; le charge de l'espèce



$\Delta_r G^\circ(\text{r}) = -RT \ln K_s(\text{r})$

$\Delta_r G^\circ(\text{r}) = -RT \ln K_s(\text{r})$

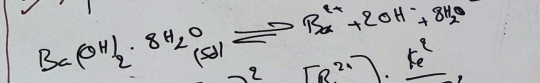
$K_s(\text{r}) = \exp - \frac{\Delta_r G^\circ(\text{r})}{RT}$

$\Delta_r G^\circ(\text{r}) = \left(\mu_{\text{Ba}^{2+}}^\circ + 2\mu_{\text{OH}^-}^\circ + 8\mu_{\text{H}_2\text{O}}^\circ \right) - \left(\mu_{\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}}^\circ \right)$

$K_s(298) = \exp - \left(\frac{\mu_{\text{Ba}^{2+}}^\circ + 2\mu_{\text{OH}^-}^\circ + 8\mu_{\text{H}_2\text{O}}^\circ - \mu_{\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}}^\circ}{R(298)} \right)$

$K_s(298) = 2 \cdot 10^{-4}$

3) a) pH de début de précipitation de $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$



$K_s = [\text{Ba}^{2+}][\text{OH}^-]^2 = [\text{Ba}^{2+}] \cdot \frac{K_e}{[\text{H}^+]^2}$

$[\text{H}^+] = \left(\frac{[\text{Ba}^{2+}] K_e}{K_s} \right)^{\frac{1}{2}}$; Au début de la précipitation $[\text{Ba}^{2+}] = C_{\text{Tba}}$

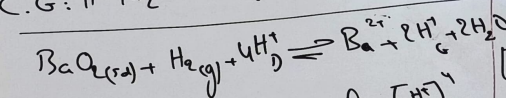
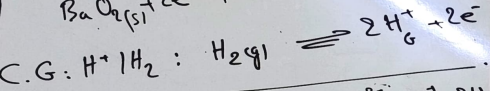
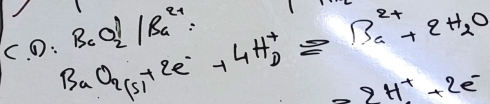
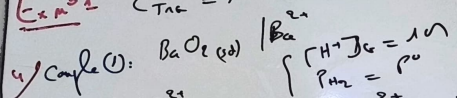
$[\text{H}^+] = \left(\frac{C_{\text{Tba}} \cdot K_e}{K_s} \right)^{\frac{1}{2}}$

$-\log[\text{H}^+] = \text{pHeq} = \text{p}K_e - \frac{1}{2} (\log C_{\text{Tba}} + \text{p}K_s)$

b) AN : $\text{pHeq} = 12,65$

$R = 8,314 \text{ J.K}^{-1}\text{mol}^{-1}$ **Serie E-pH**

Ex 1 $C_{T\text{Ba}} = 10^{-1} \text{ mol.L}^{-1}$

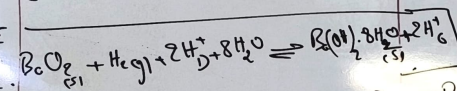
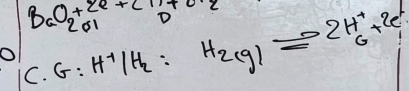
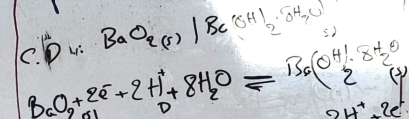
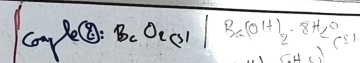


$E_1^{(\text{N.I.E.S.H})} = E_1^0 + \frac{0,06}{2} \log \frac{[\text{H}^+]^4}{[\text{Ba}^{2+}]}$

Convention de la fonction ①, $(\text{Ba}^{2+}) = C_{T\text{Ba}}$

$E_1 = E_1^0 - 0,03 \log C_{T\text{Ba}} - 0,12 \text{ pH}$

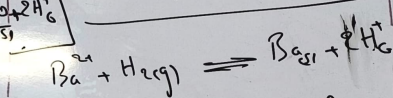
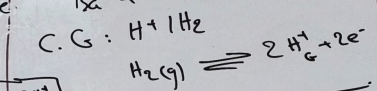
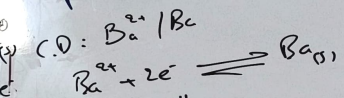
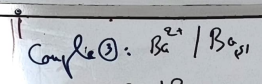
$E^{(\text{N.I.E.S.H})}_{\text{BaO}_2 / \text{Ba}^{2+}} = 2,38 - 0,12 \text{ pH}$



$E_2^{(\text{N.I.E.S.H})} = E_2^0 + \frac{0,06}{2} \log [\text{H}^+]^2$

$E_2 = E_2^0 - 0,06 \text{ pH}$

$E^{(\text{N.I.E.S.H})}_{\text{BaO}_2 / \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}} = 1,63 - 0,06 \text{ pH}$

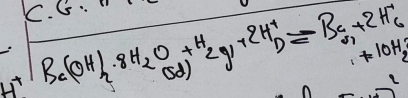
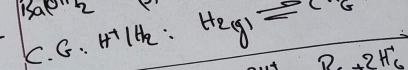
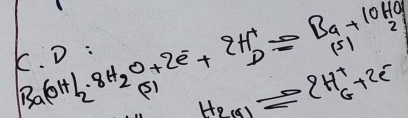
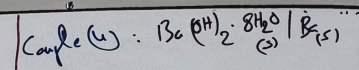


$E_3^{(\text{N.I.E.S.H})} = E_3^0 + \frac{0,06}{2} \log (\text{Ba}^{2+})$

Convention de la fonction: $(\text{Ba}^{2+}) = C_{T\text{Ba}}$

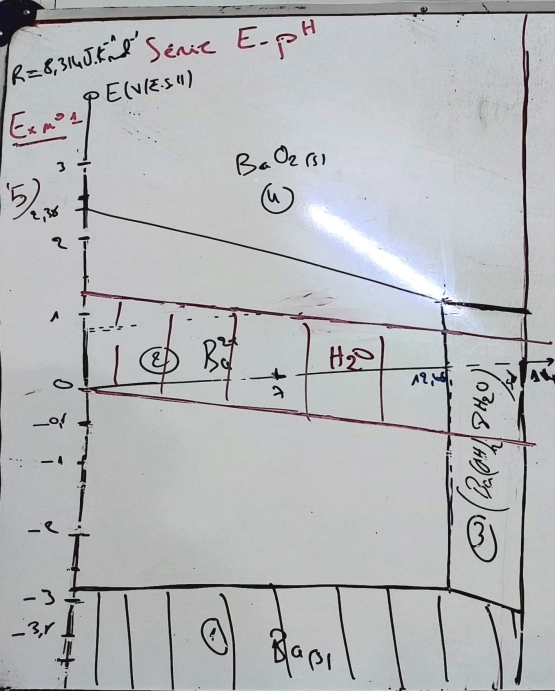
$E_3 = E_3^0 + 0,03 \log C_{T\text{Ba}}$

$E^{(\text{N.I.E.S.H})}_{\text{Ba}^{2+} / \text{Ba}} = -2,91 - 0,03 = -2,94$



$E_4 = E_4^0 + \frac{0,06}{2} \log [\text{H}^+]^2$

$E^{(\text{N.I.E.S.H})}_{\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} / \text{Ba}_{\text{gr}}} = -2,19 - 0,06 \text{ pH}$



$E_1(p^H = 12,61) = 0,86$

$E_2(p^H = 14) = 0,79$

$E_4(p^H = 14) = -3,03$

domaine (1): domaine d'existence de $(\text{Ba})_{\text{s}}$

domaine (2): domaine de prédominance de Ba^{2+}

domaine (3): domaine d'existence de $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

domaine (4): domaine d'existence de $\text{BaO}_2(\text{s})$

zone d'immunité: domaine (1)

zone de corrosion (Ba^{2+}) : domaine (2)

zone de passivation: { oxyde: BaO_2 ou BaO
hydroxyde $\text{Ba}(\text{OH})_2$ sd

zone de passivation: domaine (3) + domaine (4)

diagramme E-pH de l'eau

Couple (a): $\text{H}_2\text{O} / \text{H}_2$: H^+ / H_2 : $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$

$E_a = E_a^0 + \frac{0,06}{2} \log \frac{[\text{H}^+]}{\frac{P_{\text{H}_2}}{P_0}}$

$E_a = -0,06 \text{ pH}$

$E_{\text{H}^+/\text{H}_2}^0 = 0\text{V}$

$E_{\text{O}_2/\text{H}_2\text{O}}^0 = 1,23$

Couple (b): $\text{O}_2 / \text{H}_2\text{O}$: $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O}$

$E_b = 1,23 + \frac{0,06}{4} \log \frac{P_{\text{O}_2}}{P_0} \cdot [\text{H}^+]^4$

$E_b = 1,23 - 0,06 \text{ pH}$